ORTHOPYROXENE CHRONOMETRY OF METEORITES: I. EXPERIMENTAL DETERMINATION OF THERMODYNAMIC AND KINETIC PARAMETERS;

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Introduction: The Fe^{2+}-Mg ordering between the M1 and M2 sites of orthopyroxene has been shown to be a very important recorder of its cooling rate in a wide variety of meteoritic and terrestrial samples [1,2,3]. However, the method is very sensitive to errors in the determination of the site occupancies of the cations. Further, there are still significant gaps in the thermodynamic and kinetic data that are required to calculate cooling rate from the ordering state, especially for low Fe-compositions that are common in meteorites. In this work, we have (a) tested different crystal structure refinement techniques for the determination of site occupancies in orthopyroxenes, (b) determined the *equilibrium* intracrystalline fractionation (**k_D**) of Fe and Mg as a function of temperature and composition, and (c) determined the kinetic parameters governing the order-disorder process in an orthopyroxene crystal (Fs_{49}) separated from a terrestrial rock. Work on the kinetics of Fe-Mg order-disorder in an orthopyroxene (Fs_{15}) separated from the Steinbach meteorite is in progress, and would lead to the refinement of compositional effect on the kinetic parameters [4,5].

Determination of k_D as f(T,X): A *spherically grounded* orthopyroxene crystal (Fs_{15}) from the Steinbach meteorite was annealed at several temperatures at fO_2 = WI buffer to determine **k_D** as f(T). The equilibrium site partitioning was tightly reversed by both ordering and disordering experiments (Fig. 1), and determined by crystal structure refinement subject to bulk compositional constraints. In earlier X-ray studies [2,6,7], only reflections with $I > 3\sigma(I)$ were selected and given equal weight in the structure refinement. In addition to this procedure, we also carried out structure refinement using all reflections and weighting them properly. The weighted refinement was carried through the well known program Shell-X [8], using both ionic and atomic scattering factors. Following Ganguly et al. [2], Fe and Mn were treated as a single component.

After deletion of the outliers, the results of the site occupancy determination using the atomic scattering factors are found to be almost identical to those obtained using the ionic scattering factors, but the latter procedure always yielded smaller number of outliers. In most cases, the results from the weighted and unweighted refinement did not differ significantly, but the latter always resulted in smaller standard deviation (≤ 0.002) of the site occupancy (each site has a total of 1 cation). Based on these observations, *we recommend the use of ionic scattering factor and inclusion of all reflections with appropriate weights in the structure refinement procedure.*

We have also re-refined the X-ray data obtained by Molin et al. [6] after annealing an OPx crystal (Fs_{25}) separated from Johnstown meteorite at several temperatures between 700 and 1000^oC. In this case also, the equilibrium site partitioning was tightly reversed at each temperature. The results obtained from the weighted and unweighted refinements were found to be essentially in agreement with each other and also with those of Yang and Ghose for a synthetic OPx with Fs_{25} (Fig. 1).
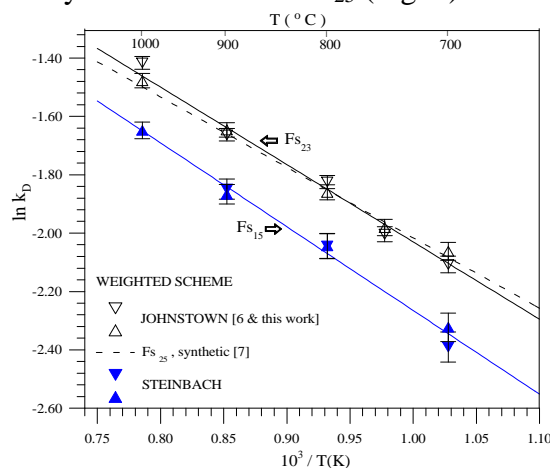

Fig 1. : Calibration of Fe-Mg site partitioning as a function of temperature and composition. Upward and downward triangles: disordering and ordering experiments, respectively.

The above calibrations yield the following relation, which can be used to determine the closure temperature (T_C) of the quenched cation ordering states for OPx composition

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.with Fs~15-25%, which are common in meteorites:

$$\ln k_D = -(3200-2190X_{Fe})/T(K) + 582 + 0.16X_{Fe},$$

where $k_D = (Fe^*/Mg)^{M1}/(Fe^*/Mg)^{M2}$, $X_{Fe} = Fe^*/(Fe^*+Mg)$, and $Fe^* = Fe+Mn$. The small amount of non-binary components present in meteoritic orthopyroxene crystals do not seem to have any significant effect on k_D. *The cooling rate can be directly retrieved from T_C using a simple analytical relation formulated in the part II.*

Kinetics of Fe-Mg order-disorder: The rate of change of site occupancy of an orthopyroxene crystal (Fs$_{49}$) was determined at 550, 650 and 750 ^oC at fO$_2$ defined by WI buffer by both ordering and disordering experiments (Fig. 2).
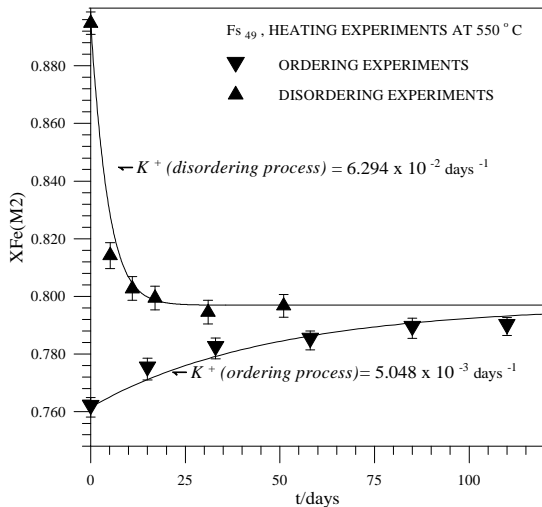

Fig. 2: Change of site occupancy of an OPx crystal (Fs$_{49}$) as a function of time at 550 ^oC. K^+: disordering rate constant.

The kinetic process was treated according to Mueller [1,9] in terms of a chemical exchange reaction:

$$Fe(M2)+Mg(M1) \underset{K^-}{\overset{K^+}{\rightleftharpoons}} Fe(M1)+Mg(M2)$$

The forward rate constant K^+, was retrieved form the results of both ordering and disordering experiments. Our results show that although K^+ derived from the two types of experiments are very similar at 650 and 750^oC, there is significant difference in their values at 550 ^oC (Figs. 2 and 3).
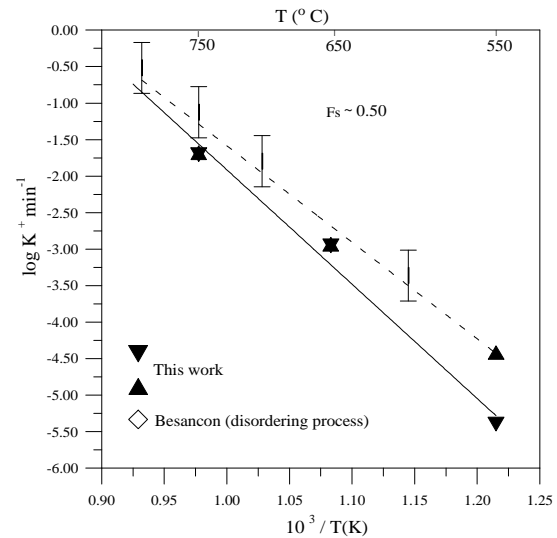

Fig. 3: Arrhenian plot of disordering rate constant, K^+. Upward and downward triangles: ordering and disordering experiments, respectively. Solid and dotted lines: regression for ordering and disordering data (including those of Besancon), respectively; fO$_2$ ~ WI buffer.

The K^+ *(disordering process)* data derived in this work are in good agreement with that of Besancon [4] for an OPx of similar composition (Fs$_{51}$), but our K^+ *(ordering process)* is much slower than those of Anovitz et al., [10]. Additional experiments are in progress at 600 ^oC to refine the Arrhenian expression of K^+ associated with both ordering and disordering process. An optimized relation for K^+ *(disordering process)*, incorporating Besancon's data for Fs$_{51}$ and Fs$_{13}$, and 1/6 power dependence on fO$_2$ is as follows:

$$\ln K^+ = 23.507+6.587X_{Fe}+ 0.167\ln(fO_2/fO_2(WI))-30445/T (K), \text{ min}^{-1}.$$

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